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(54) FIREPROOFING PAINT COMPOSITION

(71) We, CHEMIE LINZ AKTIENGESELLSCHAFT, an Austrian body corporate of, St. Peter-Strasse 25, 4020 Linz, Austria, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a foamable composition suitable for use in multicomponent fireproofing paint compositions and to a process for protecting building materials against damage by fire.

It is known to protect building materials for which fire constitutes a hazard, for at least a certain period of time, against damage in the event of a fire, by the application of protective paints. This is done in the hope that the time gained by the protective paint allows measures to be taken which either prevent the occurrence of major damage or at least substantially reduce such damage.

One of the technically most suitable means of realising an effective fireproofing paint is a formulation of such type that in the event of a fire the paint coat foams up and forms a layer of foam which is as effective as possible, that is to say which is as poor a heat conductor as possible, and which thereby screens the article beneath the coat from becoming hot excessively rapidly.

Such a flameproofing paint which forms a layer of foam is, for example, a combination of dicyandiamide with a solid alcohol, an ammonium phosphate, a polyvinyl acetate homopolymer dispersion containing trichloroethyl phosphate serving as a binder.

In practical use it is customary depending upon the nature of the article to be protected against fire, to provide the article with a rustproofing or rotproofing primer coat, which at the same time is the adhesion primer for the actual fireproofing paint which itself has to be applied in several coats to give the necessary coating thickness without dripping. However, this entails relatively high labour costs. Furthermore, it is customary to protect this expandable coat with a top lacquer.

Furthermore, these known paint compositions have not been completely satisfactory in respect of their fireproofing action.

It has further been disclosed in United States Patent Specification No. 3,574,644 that plastics materials, such as polyesters, epoxides or polyolefines, may be rendered more flameproof by the addition of expandable graphite. If this material is added to customary paints or coating compositions, they then may be used to coat flammable materials, such as timber, as well as non-flammable materials, such as metal, for insulating purposes. For this purpose, the paint is applied and heated briefly so that, as a result of the expansion of the graphite, a relatively thick insulating protective layer is obtained.

This form of protection has the disadvantage that on the one hand the paint coat requires a relatively large amount of space whilst, on the other hand, it has a low mechanical strength so that it may be damaged by slight blows.

The present invention provides a pain composition based on expandable graphite which, similarly to the known paint compositions, only develops its insulating action, by expansion, in the event of a fire

but which even then still has such mechanical strength that the paint does not flake off, and hence lose its protective action, as a result of the fire draught or other mechanical stress. According to the present invention it has proved possible to achieve this by using a two-compound binder system, of which one provides a tacky bond whilst the other, in the event of a fire, as a result of decomposition which depends upon the temperature, forms a carbon skeleton which provides a hold for the expanded graphite.

Accordingly, the present invention provides a foamable composition chosen to provide fire protection when used to form an intermediate layer in a three-layer fireproof coating on a substrate, which composition comprises predominantly or entirely (a) expandable graphite capable of expanding to 10 to 40 times its initial volume, (b) a tacky polychloroprene which has been partially degraded by mastication, a chlorinated rubber and/or chlorinated polyolefin and (c) one or more phenolic resins which show thermoplastic behaviour up to a temperature of at least 200°C, the components (b) and (c) being present in a proportion of 10 to 50 parts by weight per 100 parts by weight of expandable graphite.

In the three component pack the primary function of the primer coat is to ensure adequate adhesion to the substrate to which the fireproofing paint is applied. Where the substrate is of a material which is subject to corrosion or rotting the primer selected will usually be one containing components which inhibit or prevent corrosion or rotting. Thus in the case of steel building materials where rustproofing is of considerable importance the primer selected will usually be a passivating and rustproofing primer such as are well known. Where the substrate is wood the primer will usually be rot-proofing primer containing anti-microbial (including anti-fungal components. Such primers are well known. It is important, and therefore highly preferred, that this primer coat should adhere well to the substrate and should be readily compatible with the fireproofing active coat to be applied on top of it, that is to say it should provide a stable adhesion primer for the latter even in the event of a fire.

The intermediate coat is the actual fireproofing active coat. The expandable graphite contained therein, component (a) expands greatly on heating, with elimination of a little water vapour and traces of nitrous gases. The increase in volume is 10 to 40 times, preferably 15 to 20 times, the initial volume.

The process of expansion starts at or just below 150°C, takes place initially almost violently and then more slowly, and terminates not later than reaching a temperature of 600°C. A loose, moss-like layer of graphite lamellae swollen to resemble small sausages remain. This layer has an excellent insulating action in preventing the passage of heat.

The following literature references which deal with "expandable graphite", its manufacture and its properties, should be mentioned:

1. Schafhäutel: Journal f. prakt, Chemie 21 (1841), page 155.
2. Brodie: Liebigs Annalen 114 (1860) page 6.
3. Luzi: Bericht d. deutschen chem. Ges. 24 (1891) Volume II page 4,085.
4. Hofmann and Frenzel: ibid. 63 (1930), page 1,249.
5. Thiele: Zeitschr. f. anorg, u. allgem. Chemie 67 (1932) page 340.

Industrially, "expandable" graphite is manufactured almost exclusively by the brief treatment of coarsely flocculent natural graphite with highly concentrated nitric acid. The product is then washed until neutral and dried carefully at a temperature of 80°C.

The following laboratory method was used to measure the increase in volume on expansion of the graphite:

5 to 10 g of graphite were weighed out accurately into a nickel dish of 450 to 500 ml volume. The sample is placed in a calcining furnace at 500°C for 30 minutes. The calcined sample is introduced into a measuring cylinder and the cylinder containing the sample is tapped against a solid support until there is no further change in volume. A blank volume measurement is carried out by the same procedure on the unexpanded graphite.

$$\text{Increase in volume on expression} = \frac{\text{ml of tapped volume of expanded graphite/g}}{\text{ml of tapped volume of unexpanded graphite/g}}$$

The following are used as component (b), which should provide a tacky elastic bond:

1. Polychloroprene (degraded by mastication to the point that it becomes tacky and that the viscosity of non-aqueous solutions of the material is not excessively high)
2. Chlorinated rubber or
3. Chlorinated polyolefine plastics materials such as, for example,

chlorinated polyethylene or polypropylene, it is also being possible for mixtures of these substances to be present.

However, this component leaves no coke in the event of a fire.

The latter task is fulfilled by the phenolic resin employed as component (c), the following phenolic resins being particularly suitable:

1. Phenolic resins modified with natural resin.
2. Phenolic resins modified with hydrocarbons, e.g.
   (a) phenol-terpene resins
   (b) phenol-acetylene condensates
   (c) phenol condensates with hydrocarbon-formaldehydye resins.
3. Phenolic resins modified with linseed oil or wood oil by boiling.
4. Novolac-like products, such as are produced from the alkali-catalysed reaction between furfuraldehyde and phenols (particularly alkyphenols).
5. Phenyl allyl ether resoles.
6. Condensates of phenols with benzyl chloride.

A shared feature of all these phenolic resins is that they show purely thermoplastic behaviour at least up to 200°C, that is to say they do not hinder the process of expansion of the "expandable" graphite. At even higher temperatures, the resins mentioned either change gradually into coke without prior curing or they undergo a partial curing process which, however, in no way leads to rigid highly cross-linked thermosetting resins, such as are obtained from phenol-formaldehyde resoles. This also applies to those of the abovementioned resin types which are of resole character.

The preparation of a binder suitable for the "expandable" graphite, is suitably carried out as follows:

25 to 75 parts by weight of at least one of the elastomer-like halogen-containing polymers mentioned above and 75 to 25 parts by weight of at least one of the phenolic resins mentioned above are dissolved in a suitable solvent or solvent mixture. As such it is possible preferentially to use a hydrocarbon, for example, toluene, solvent naptha or white spirit, or a ketone or ester. Understandably, it is desirable to accommodate in these binder solutions as large an amount of dissolved matter as possible, but this desideratum is limited, on the one hand, by the solubility of the materials and, on the other hand, by the viscosity of the solution obtained. As regards the optimum viscosity of the binder solution, a flow time of the latter of between 30 and 60 seconds, measured by means of a Ford cup with nozzle No. 8 at 22°C, is to be recommended. Correspondingly, the solids concentration the solution in most cases is between 20 and 30% by weight.

To prepare the fireproofing paint, which is best done immediately before use, "expandable" graphite is stirred with sufficient binder solution to provide 10 to 50 parts by weight of binder (calculated as solvent-free solid) per 100 parts by weight of expandable graphite. A pasty mass is obtained, which may be applied to the articles which are to be protected and have been provided with a primer coat, by trowelling or preferably by means of special spray guns. Such application is also possible without difficulty on vertical surfaces since the pasty consistency of the material, which is very thixotropic because of the coarsely lamellar graphite contained in it, prevents the formation of runs or "tear-drops". For this reason, it is also possible to apply the desired thickness of coat all at once, that is to say it is not necessary to apply several coats with drying intervals between them. The optimum coating thickness of the fireproofing coat is preferably 2±1 mm (in the fully dried but unexpanded state).

The top paint coat, which is preferably applied to the previously fully dried foam-forming coat, serves the following purposes:—

(i) Protection of the paint coats beneath it against the action of water (for example rain) and other atmospheric factors and additionally, where appropriate, protection against corrosive factors of other kinds;

(ii) best possible protection against damage under moderate mechanical stresses;

(iii) provision of a base for decorative coatings, which may be desired if the fireproofing coat is to be applied to visible surfaces, and, finally;

(iv) in the event of a fire, formation of a firmly adhering, stiff covering crust which it is essential should be microporous to permit the passage of pyrolysis gases and vapours which are evolved from the coats of the fireproofing paint system beneath the top coat. The formation of a crust is necessary to that the loose, heat-insulating expanded graphite coat is not blown away by the draught caused by the gases of the fire, that is to say by the "flue action".

In order to comform to the above requirements as extensively as possible it is best to select slightly reactive or "self-curing" paint compositions with inorganic-silicate or organic-silicate binders; these compositions are already in themselves known, but if subjected to modification by the addition of "pore-forming agents" offer

advantages for the particular application under discussion here.

Top coats based on waterglass are weather-resistant after they have set and proved adequate in most cases even though they contain small amounts of alkali metal carbonate. These coats are based on commercially available highly concentrated solutions (25 to 30% solids content) of alkali metal silicates ("waterglass"). The use of potassium waterglass is preferred. Since alkali metal carbonates which may be present are water-soluble, potassium waterglass compositions of lowest possible alkali content are preferred, particularly those with a SiO_2:K_2O ratio of 3.5 to 4.0. However, where complete freedom from alkali is required in special cases, esters of polysilicic acids are used for the top coat. Methyl polysilicates and ethyl polysilicates which may be obtained by controlled partial saponification of tetraalkyl orthosilicic acid esters are the most advisable to use for this purpose.

Reactive metal powders, oxides or hydroxides, (basic) carbonates, borates and, if appropriate, phosphates should be added to the top coat (regardless of whether it is based on waterglass or silicic acid esters); these additives, after not excessively long "setting time" (1 to 6 hours), form water-insensitive silicate coats which in the event of a fire sinter together to form a firm but micro-porous (and therefore gas-permeable) crust.

The following may be mentioned as preferred reactive additives to the silicate binder:— very finely divided zinc dust ("paint-grade zinc dust"), zinc oxide, zinc borate, magnesium oxide, magnesium hydroxide, basic magnesium carboate, aluminium hydroxide, lead oxide (both "litharge" and "red lead") and white lead carbonate).

Furthermore, when coloured top coats which produce a decorative effect are desired, it is possible to add pigments which are stable in the medium concerned and are preferably inorganic. As examples of these there may be mentioned carbon black, ultramarine, chrome yellow, chrome oxide green, ochre and iron oxide pigments of various colour shades.

Furthermore, it is advantageous to add "pore-forming agents" to the top coat according to the invention, in addition to the "reactive" additives just mentioned. These pore-forming agents serve the purpose of producing a large number of micro-pores in the silicate top coat even starting at temperatures from 100° to 150°C (that is to say below the temperature range in which gases and vapours are evolved from the graphite coat which begins to expand). These additives are intended to permit adequate of gas and hence to prevent the top coat from splitting open and/or flaking off from the expanded graphite heat-insulating coat. Suitable "pore-forming agents" are pulverulent materials having a particular size less than 250 μ, preferably 50 to 150 μ, which do not react with the binder of the top coat (waterglass or polysilicic acid ester) and also do not dissolve therein. Furthermore, the "pore-forming agents" must be capable of forming an appropriate micro-pore system in the top paint coat at temperatures from 100° to 150°C, preferably 120°C, either by melting or by shrinkage or decomposition. The following may be mentioned as illustrative examples of suitable pore-forming agents:— thermoplastic synthetic resins which melt at not more than 150°C. e.g. polyvinyl chloride, polyethylene and ethylene/vinyl acetate copolymers; phenol-formaldehyde condensates of the novolac type, natural resins, wood flour and short-fibre asbestos (maximum fibre length 2 mm).

Conventional blowing agents such as, for example, benzene-sulphonic acid hydrazide, also may be used. However, in that case the amount must be chosen very carefully and particularly finely divided preparations must be used since the above compound and similar "blowing agents" form a considerable volume of gas through rapid decomposition within a narrow a range, and this may have a thoroughly undesirable effect on the top coat, causing it to flake off.

The above fire-protection paints are tested on steel building materials in accordance with DIN 4102, page 2, paragraph 5, and to obtain official certification of a particular category of fire resistance in the burning test, the conditions stated in the above specification, page 2, paragraph 3. 1. 1. 2, have to be fulfilled.

The making-up and practical use of a fireproofing paint composition according to the invention is illustrated in following Examples.

Example 1

A steel sheet of size 500x500 mm and 4 mm thickness is cleaned carefully to remove any adhering rust and other impurities and is slightly surface-roughened in a known manner by sand-blasting. In most cases, the cleaning of the surface is superfluous in view of the sand-blasting which has to be carried out in every case. The sheet is then immediately primed with metal primer (anti-corrosion primer coat).

After 12 hours, when the primer coat has dried thoroughly, the fireproofing coat, comprising equal parts by weight of

"expandable" graphite and paint binder is applied. The following conditions apply with regard to the individual components of this coat:—

1. The "expandable" graphite is completely neutral and dry. The particle size of the graphite lamellae is predominantly in the range from 1.5 to 3.0 mm. The graphite used has an expandability of 18 times the initial volume.

2. The binder is prepared as follows:

(a) first, unvulcanised polychlorobutadiene is degraded by mastication until a 25% strength solution of the material has a viscosity in toluene which corresponds to a flow time of 45±5 seconds from a Ford cup with nozzle No. 8 at 22°C. 10 parts by weight of this degraded polychlorobutadiene together with 5 parts weight of

(b) thermoplastic phenol-terpene condensation resin are dissolved in 40 parts by weight of toluene, whilst stirring well. The said phenol-terpene resin is selected from commercially available products (for example those known under the registered Trade Marks "Durez" and "Alresen").

(c) Finally, 5 parts by weight of a novolac-like condensate of 2 mols of isononylphenol and 1 mol of furfuraldehyde, which has been prepared under the influence of an alkaline catalyst (see Houben-Weyl: "Methoden der organischen Chemie" ("Methods of Organic Chemistry"), Volume 14/2 (Macromolecular Substances II) on page 281, Example 28) is dissolved in 10 parts by weight of hot butyl acetate and the solution is diluted with 10 parts by weight of toluene.

(d) The solution which consists of the components described above under (a) and (b) is then combined with the solution according to (c) and the mixture is diluted with 20 parts by weight of benzine of boiling range 80° to 120°C. The benzine must be admixed slowly, with good stirring, to obtain a homogeneous stable solution.

In total, the binder thus prepared accordingly consists of:

10 parts by weight of masticated polychlorobutadiene	20%
5 parts weight of phenol-terpene resin	solids
5 parts by weight of phenol-furfuraldehyde novolac	80% solvent
50 parts by weight of toluene	
20 parts by weight of benzine	
10 parts by weight of butyl acetate	

The viscosity of this binder corresponds to a flow time of 41 seconds measured by means of a Ford cup (nozzle No. 8, 22°C).

3. The fireproof coat.

Shortly before use, equal parts by weight of "expandable" graphite and binder are very thoroughly mixed with one another. A pasty thixotropic mass results, which is applied to the previously thoroughly dried primer coat. The fireproof coat is applied in a single pass by means of a spray gun of 3 mm nozzle width, and is smoothed manually with a roller to even out the thickness of the coat. After drying, the average thickness of the coat is 2.0 mm.

4. The top coat.

the following components are mixed:—

(a) 60 parts by weight of potassium waterglass (molar ratio SiO_2:K_2O=3.8, concentration approx. 25% solids) is mixed as homogeneously as possible with 5 parts by weight of very fine wood flour ("pore-forming agent").

(b) 5 parts by weight of zinc oxide is extremely thoroughly worked into a paste with 10 parts by weight of aluminium hydroxide, 20 parts by weight of finely powdered chalk and a little water, to give a homogeneous paste.

The two constituents components (a) and (b) are mixed in equal parts by weight immediately before use. This top protective paint is also applied by means of a spray gun.

The coated metal sheet is tested in accordance with DIN 4102, page 2 "minor Fire Test". The average value of 9 temperature measurements on the side facing away from the fire must not exceed 400°C. and no indvidual value must exceed 500°C. The fire resistance category is quoted in accordance with the period of time required to reach these limiting values. In two parallel experiments, the limiting value in one case is reached after 90 minutes and in the other case after 100 minutes.

Example 2

A steel building panel as described in Example 1 is primed with a zinc chromate primer as a corrosion protection and a fire-proofing coat of the following composition is applied:

40 parts by weight of "expandable" graphite (as in Example 1) and

60 parts by weight of a commercially avilable synthetic resin mixture consisting of polychlorophene, phenolic resin and terpene-phenol resin dissolved in toluene/benzine/ethyl acetate such as that described under the code KF-2174 by Union Carbide Corporation.

After 36 hours, the fireproofing coat is thoroughly dried, after which the top paint coat is applied.

This is prepared from:—

Component A

60 parts by weight of ethyl polysilicate, 30 parts by weight of zinc borate containing water by crystallization (zinc borate 2335 Borax Consolidated), 10 parts by weight of aluminium hydroxide, 1 part by weight of polyvinyl chloride powder.

Component B

30 parts by weight of 90% strength technical-grade alcohol, in which are dissolved

1 part by weight of anhydrous zinc chloride and

1 part by weight of mannitol.

The two components A and B are stirred before use and applied by means of a spray gun.

WHAT WE CLAIM IS:—

1. A foamable composition chosen to provide fire protection when used to form an intermediate layer in a three-layer fireproof coating on a substrate, which composition comprises predominantly or entirely (a) expandable graphite capable of expanding to 10 to 40 times its initial volume, (b) a tacky polychloroprene which has been partially degraded by mastication, a chlorinated rubber and/or chlorinated polyolefin and (c) one or more phenolic resins which show thermoplastic behaviour up to a temperature of at least 200°C, the components (b) and (c) being present in a proportion of 10 to 50 parts by weight per 100 parts by weight of expandable graphite.

2. A composition according to claim 1, in which component (c) is a phenolic resin modified by hydrocarbons, linseed oil or wood oil.

3. A composition according to claim 1, in which component (c) is a novolac-like product of an alkali-catalysed reaction of furfuraldehyde and a phenol.

4. A composition according to claim 3, in which the said phenol is an alkylphenol.

5. A composition according to claim 1, in which component (c) is a phenyl allyl ether resole or a condensate of phenol with benzyl chloride.

6. A three-component fireproofing paint pack comprising (i) an adhesion-promoting primer paint, (ii) a composition according to any one of claims 1 to 5 and (iii) a top paint chosen to provide a protective coat over an intermediate layer provided by composition (ii).

7. A pack according to claims 1 to 6, in which the top paint comprises a slightly reactive self-curing paint composition containing an inorganic-silicate or organic-silicate binder.

8. A pack according to claim 7, in which the top paint contains water-glass or an ester of a polysilicic acid, and one or more reactive metal powders, metal oxides or hydroxides, basic metal carbonates, borates and/or phosphates, which will form a water-insensitive silicate coat with the silicon compound.

9. A pack according to claim 7 or 8, in which the basic component of the top paint is potassium waterglass have an SiO_2:K_2O ratio of 3.5 to 4.0.

10. A pack according to claim 7 or 8, in which the basic component of the top paint is an ester of a polysilicic acid.

11. A pack according to claim 10, wherein the said component is a methyl polysilicate and/or ethyl polysilicate.

12. A pack according to any one of claims 7 to 11, in which the top paint contains a pore-forming agent of particle size less than 250 μ, which does not react with or dissolve in the silicate base and is capable of forming pores at temperatures from 100° to 150°C by melting, shrinkage or decomposition.

13. A pack according to claim 12, in which the pore-forming agent has a particle size of 50 to 150 μ.

14. A pack according to claim 12 or 13, in which the pore-forming agent is a thermoplastic synthetic resin which melts at not more than 150°C, a phenol-formaldehyde condensate of the novolac type, a natural resin, wood flour or asbestos fibre.

15. A pack according to any one of claims 7 to 14, in which the top paint contains a non-ionic hydrophilic, surface-active agent.

16. A process for protecting building materials which are sensitive to fire against the action of a fire, by means of a pack according to any one of claims 7 to 15 which comprise applying to the material to be protected a coat of the corrosion-proofing or rot-inhibiting adhesion-promoting primer paint and then coating the material, preferably in a single step, with a foamable composition to any one of claims 1 to 5, and finally, after thorough drying, applying a coat of the top paint.

17. A process according to claim 16, in which the thickness of the foamable intermediate coat is 1 to 3 mm.

18. A foamable composition according to claim 1 and substantially as hereinbefore described with reference to the Examples.

19. A fireproofing paint pack for building materials which are sensitive to fire according to claim 6 and substantially as hereinbefore described with reference to the Examples.

20. A fireproof article of metal or timber which is provided with a coat formed from a pack according to any one of claims 6 to 15 or 19.

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